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(54) Silicon carbide sintered article and process for its production

(57) A silicon carbide sintered article consisting essentially of silicon carbide; from 0.5 to 35% by weight, as calculated as Al relative to the silicon carbide, of Al and/or a refractory Al compound; and from 2 to 99% by weight, relative to the silicon carbide, of at least one boride selected from borides of elements belonging to Groups 4A, 5A and 6A in the 4th, 5th and 6th periods of the periodic table, wherein at least a half amount of silicon carbide grains is constituted by elongated and/or plate-like silicon carbide grains.

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SPECIFICATION

Silicon carbide sintered article and process for its production

5 The present invention relates to a silicon carbide sintered article. More particularly, it relates to a silicon carbide sintered article comprising an aluminum (Al) component and a boride, and a process for its production. 5

Silicon carbide is a covalently bonded compound having high hardness and rigidity, a small thermal expansion coefficient and a high decomposition temperature. A sintered article of silicon carbide has high strength at high temperatures, and it is expected to be used as a light-weight high temperature structural material having high thermal shock resistance and excellent wear resistance. 10

For the production of high density sintered articles of silicon carbide, a hot pressing method, a pressureless sintering method, a reaction sintering method and a CVD method are known. However, highly dense products are not obtainable without using a sintering additive even by the hot pressing method, not to mention the practically useful pressureless sintering method. Therefore, studies on the sintering additives have been strenuously made. 15

Heretofore, researches have been particularly active on the method for obtaining sintered articles having high strength, and it has been proposed to use boron or boron compounds and carbon as sintering additives in e.g. U.S. Patents 4,004,934 and 4,124,667. These additives have drawbacks such that the value of fracture toughness will be low and the sintering temperature is required to be high, although they have excellent characteristics such that they are capable of promoting the densification with a small amount and the strength will not deteriorate up to a high temperature. 20

On the other hand, it has been proposed to use Al_2O_3 as a sintering additive in e.g. U.S. Patent 4,354,991. The sintered article produced under the preferred conditions has high strength and a high value of fracture toughness, and is superior as a usual high temperature structural material. However, when it is used in contact with a steel material or the like at high temperatures, it is possible that a low melting-point compound (such as cementite or ferrosilicon) in Fe-Si-C system, is formed by the reaction of silicon carbide with iron. Therefore, it is not necessarily useful for applications where abrasion is involved. This drawback can not be solved even when the above-mentioned boron or boron compounds are used in a small amount as a sintering additive. 25

On the other hand, borides such as BN, TiB_2 , ZrB_2 and CrB_2 , are known as materials having high corrosion resistance against iron. However, it is difficult to obtain high density sintered products of these borides. Even if high density products were obtained, it was difficult to obtain a high value of fracture toughness with them, or the oxidation resistance was inadequate. Further, in the production of composite sintered products of these borides with silicon carbide, if these borides are added in a large amount to silicon carbide, sintering will be difficult. 30

U.S. Patent 4,327,186 proposes to produce a silicon carbide sintered article containing TiB_2 by a pressureless sintering method. However, in this method, boron and carbon are used as sintering additives, whereby it is impossible to obtain a high value of fracture toughness. Further, EP95720A and Japanese Unexamined Patent Publication No. 101702/1984 disclose silicon carbide sintered articles obtained by adding ZrB_2 or VB_2 to black silicon carbide powder having a particle size of a few micrometers to impart electric conductivity, followed by hot pressing. However, it is considered that even if Al_2O_3 is used as a sintering additive, silicon carbide grains will be equiaxed grains, whereby the value of fracture toughness will be still low. 35

The present invention is intended to solve the above-mentioned problems of the prior art. Namely, it is an object of the present invention to provide a silicon carbide sintered article having high density and high corrosion resistance while maintaining excellent mechanical properties such as high flexural strength and high fracture toughness, which yet can be formed into various desired shapes, and to provide a process for its production. 40

The present invention provides a silicon carbide sintered article consisting essentially of silicon carbide; from 0.5 to 35% by weight, as calculated as Al relative to the silicon carbide, of Al and/or a refractory Al compound; and from 2 to 99% by weight, relative to the silicon carbide, of at least one boride selected from borides of elements belonging to Groups 4A, 5A and 6A in the 4th, 5th and 6th periods of the periodic table, wherein at least a half amount of silicon carbide grains is constituted by elongated and/or plate-like silicon carbide grains. 45

The present invention also provides a process for producing a silicon carbide sintered article which comprises sintering a green body comprising silicon carbide, from 0.25 to 40% by weight, as calculated as Al relative to the silicon carbide, of Al and/or an Al compound and from 2 to 120% by weight, relative to the silicon carbide, of at least one boron compound selected from boron compounds of elements belonging to Groups 4A, 5A and 6A in the 4th, 5th and 6th periods of the periodic table, in a vacuumed atmosphere or in a non-oxidizing atmosphere under a pressure of not higher than 10 atm at a temperature of from 1800 to 2300°C. 50

Now, the present invention will be described in detail with reference to the preferred embodiments. 55

The silicon carbide sintered article of the present invention is composed basically of the following three components. The first component is silicon carbide. The second component is Al and/or a refractory Al 60

compound. The third component is at least one boride selected from borides of elements of Groups 4A, 5A and 6A in the 4th, 5th and 6th periods of the periodic table, i.e. titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), and tungsten (W).

The silicon carbide sintered article of the present invention is preferably composed solely of the three components, but may contain other components in small amounts not to impair the object and effects of the present invention. Further, even when the article is composed essentially of these three components, it may contain very small amounts of impurities such as Fe, etc. e.g. derived from the starting material silicon carbide powder or unavoidable impurities attributable to the starting materials, such as SiO_2 contents attributable to the oxidized surface of the starting material silicon carbide powder, or unavoidable impurities included during e.g. the pulverization or mixing process for the starting material powders.

Al and/or a refractory Al compound of the second component serves as an agent for promoting the sintering and, in particular, serves to control the structure of silicon carbide grains in the sintered article. The Al compound includes a compound such as aluminum hydroxide or aluminum isopropoxide, which undergoes pyrolysis to release water and organic components and to be converted into Al_2O_3 (alumina) which is stable at high temperatures. The refractory Al compound in the present invention means an Al compound which is stable at high temperatures, such as Al_2O_3 . The refractory Al compound further includes AlN , Al_4C_3 , aluminum oxynitride (such as $\text{Al}_{23}\text{O}_{27}\text{N}_5$) and AlB_2 . However, as the second component of the present invention, Al and/or Al_2O_3 , especially Al_2O_3 , is preferred in view of the availability and handling efficiency of the raw material.

The second component is contained in an amount of from 0.5 to 35% by weight (hereinafter indicated simply by "%" unless otherwise specified) as calculated as Al relative to the silicon carbide of the first component. If the second component exceeds 35%, it is likely that the high temperature strength or the thermal shock resistance deteriorates. It is preferably not higher than 25%. If it is less than 0.5%, the sintering tends to be difficult. It is preferably at least 1.0%. It is more preferably from 3.5 to 15% so that the sintered article has particularly good physical properties. The term "as calculated as Al" means, for example, that when Al_2O_3 is 10% relative to the silicon carbide, it is 5.3% as calculated as Al.

The above-mentioned borides of the third component are considered to have a function to improve the overall corrosion resistance of the sintered article against e.g. iron. It is considered that in a non-oxidizing atmosphere, their inherent nature of being hardly wettable with e.g. iron serves to prevent the reaction of silicon carbide with e.g. iron.

As such borides, TiB , TiB_2 , ZrB , ZrB_2 , HfB_2 , V_3B_4 , Nb_3B_4 , TaB_2 , CrB , CrB_2 , MoB_2 , MoB_4 , WB_2 , WB_4 and the like may be mentioned. Among them, borides of Group 4A or 6A elements, particularly TiB_2 , ZrB_2 , CrB_2 , MoB_2 and WB_2 , are preferred since even when the sintered articles containing them are used in an oxidizing atmosphere, an oxidized layer formed on the surface will protect the interior.

Although the detailed mechanism is not known, in the case of TiB_2 , TiO_2 or FeTiO_3 formed by the reaction with iron prevents the internal silicon carbide from direct reaction with iron. In the case of ZrB_2 , ZrO_2 or ZrSiO_4 formed by the reaction with SiO_2 which is in turn formed by the oxidation of silicon carbide, exhibits high corrosion resistance against iron. In the case of CrB_2 , Cr_2O_3 exhibits high corrosion resistance against iron. In the cases of MoB_2 and WB_2 , MoO_3 and WO_3 are considered to serve as protective layers. Further, Hf has an ion radius substantially equal to that of Zr, and therefore ZrB_2 is capable of forming a solid solution with HfB_2 . The boride may be such a solid solution.

The third component is contained in an amount of from 2 to 99% relative to the silicon carbide of the first component. If it exceeds 99%, the sintering becomes extremely difficult, and the oxidation resistance or fracture toughness tends to deteriorate. Preferably, it is not high than 49%. If it is less than 2%, no adequate corrosion resistance is obtainable. Preferably, it is at least 5%. More preferably, it is from 10 to 29% to obtain a sintered article having superior properties.

The silicon carbide of the first component includes an α -form and a β -form, and it may take either form or may be a mixture of both forms in the sintered article.

Structurally, at least a half amount of silicon carbide grains in the silicon carbide sintered article of the present invention is constituted by elongated and/or plate-like silicon carbide grains.

The structure of the sintered article can be ascertained by the observation by means of an optical microscope or an electron microscope. With respect to microstructures of conventional silicon carbide sintered articles, equiaxed grains having approximately equal dimensions in all directions, elongated grains which are monoaxially elongated and plate-like grains which are monoaxially short, are known as silicon carbide crystal grains.

In the silicon carbide sintered article of the present invention, such elongated and/or plate-like grains constitute at least a half amount, preferably at least 70%, more preferably at least 90%, of the total silicon carbide grains. Such a structure is effective for preventing propagation of cracks and brings about high fracture toughness. Such elongated and/or plate-like grains preferably has an aspect ratio of at least 2.0, more preferably at least 3.0, with a view to attaining an improvement of the fracture toughness. Further, such elongated and/or plate-like grains preferably have a major axis of at least $0.5\text{ }\mu\text{m}$, more preferably at least $2.0\text{ }\mu\text{m}$, which indicates grain growth from equiaxed grains, whereby the aspect ratio will advantageously be high. If the major axis is too long, a defect is likely to be led. Therefore, the major axis is preferably not higher than $100\text{ }\mu\text{m}$, more preferably not higher than $30\text{ }\mu\text{m}$, to obtain high strength. In the silicon carbide sintered article of the present invention, the elongated and/or plate-like grains are preferably randomly oriented and

preferably mutually intercrossed so that the fracture toughness and creep rupture resistance of the sintered article are thereby improved. Further, in the silicon carbide sintered article of the present invention, the less the equiaxed grains of silicon carbide, the better. However, the equiaxed grains may be present together with the elongated and/or plate-like grains. In such a case, the equiaxed grains preferably have a grain size of not larger than 30 μm , more preferably not higher than 20 μm .

Further, in many cases, a second component phase and a third component phase are observed in the silicon carbide sintered articles of the present invention. The second component phase, such as Al_2O_3 phase, is present mostly as an intergranular phase at e.g. triple points. In some cases, it is present in the form of crystal grains having substantially the same size as the silicon carbide grains, or it is observed as a mixture of an intergranular phase and crystal grains above-mentioned. The third component phase is observed, in many cases, as crystal grains, particularly as equiaxed grains. The average grain size of the second component phase is preferably not larger than 30 μm from the viewpoint of the high temperature strength and creep rupture resistance. Likewise, the average grain size of the third component phase is preferably not larger than 15 μm from the viewpoint of the strength and corrosion resistance.

In the silicon carbide sintered article of the present invention, the silicon carbide grains, the second component phase and the third component phase are desired to be randomly and macroscopically uniformly dispersed so that the strength and corrosion resistance are uniform in the sintered article.

In the process for the production of silicon carbide sintered article of the present invention, the starting material basically comprises the following three components. The first component is silicon carbide. The second component is Al and/or an Al compound. The third component is at least one boron compound selected from boron compounds of elements belonging to Groups 4A, 5A and 6A in the 4th, 5th and 6th periods of the periodic table, i.e. Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. The silicon carbide starting material may be composed predominantly of either the α -form or the β -form, or may be a mixture of both forms. However, the β -form is preferred since it is likely to form elongated or plate-like grains while being converted to 4H-type among various types of the α -form. The starting material silicon carbide is desired to be as pure as possible. Particularly, in order not to lower the mechanical properties, the total amount of the Na content, the K content and the Ca content should not exceed 0.2%, preferably 0.05%, as calculated as metals. As mentioned above, it is also desirable that the SiO_2 content attributable to the surface oxidation is minimum.

As the second component, Al, Al_2O_3 , $\text{Al}(\text{OH})_3$, AlN, $(i\text{-C}_3\text{H}_7\text{O})_3\text{Al}$ (aluminum isopropoxide), Al_4C_3 and $\text{AlC}_{10}\text{H}_{13}\text{O}_8\text{N}_2$ (aluminum ethylenediaminetetraacetate) may be mentioned. Among them, Al, Al_2O_3 , $\text{Al}(\text{OH})_3$ and AlN are preferred, since active fine powders having excellent sinterability are readily obtainable. It is usual to employ one of them alone. However, they may be used in combination of two or more different kinds.

Such a second component is used in an amount of from 0.25 to 40% as calculated as Al relative to the silicon carbide of the first component. The numerical range is somewhat different from the corresponding proportion in the sintered article. This is due to the fact that the Al content is likely to be evaporated during the sintering process, and at the same time, it is possible to supply it from the atmosphere. The second component is preferably not more than 25%, more preferably not more than 15%. It is preferably at least 2.0%, more preferably at least 3.5%. The reason for such limitations is similar to that described with reference to the sintered article.

As the third component, various borides as mentioned with regard to the third component in the sintered article may be employed for the same reason. Further, boric acid salts such as TlBO_3 and CrBO_3 and boron compounds such as $\text{Zr}(\text{BH}_4)_4$ and $\text{H}_5[\text{B}(\text{W}_3\text{O}_{10})_4]\cdot 5\text{H}_2\text{O}$, may be used alone or in combination with the above-mentioned borides.

Such a third component is used in an amount of from 2 to 120% relative to the silicon carbide of the first component. This numerical range is somewhat different from the above-mentioned corresponding proportion in the sintered article. This is due to the fact that boron compounds other than borides may be used, and the third component itself or a part of the constituting elements of the third component is likely to be evaporated during the sintering process. The third component is preferably not more than 49%, more preferably not more than 29%. It is preferably at least 5%, more preferably at least 10%. The reason for such limitations is similar to that described with reference to the sintered article.

The starting material for the silicon carbide sintered article of the present invention is preferably composed solely of these three components so far as the components to be positively remained in the sintered article are concerned. However, the starting material may contain small amounts of other components so long as they do not impair the purpose and effects of the present invention.

Such starting materials are weighed in the respective predetermined amounts, and pulverized and mixed in a dry or wet system so as to bring the average particle size of the first component preferably to a level of not more than 0.8 μm , more preferably not more than 0.4 μm , the average particle sizes of the second and third components to a level of preferably not more than 10 μm , more preferably not more than 1 μm . If necessary, a molding binder, etc. may be added and mixed, and the mixture is formed into a green body by a suitable molding method such as a cast molding method, a press molding method, an injection molding method or an extrusion molding method.

The green body thus obtained may, if necessary, be subjected to removal of the molding binder, and then heated in a vacuumed atmosphere or a non-oxidizing atmosphere at a pressure of not higher than 10 atm at a temperature of from 1800 to 2300°C for sintering. The Al and/or the Al compound added as the second

component turns into the Al and/or the refractory Al compound during the sintering process, and at the same time a part thereof reacts with silicon carbide or SiO_2 present on the surface of the silicon carbide, to form a liquid phase. It is considered that in this liquid phase, fine silicon carbide particles repeat dissolution and precipitation, whereby elongated or plate-like grains grow, and form a microstructure having high strength and high fracture toughness. Finally, the liquid phase becomes mainly a refractory Al compound.

The boron compound of the third component undergoes thermal decomposition or reacts with the Al and/or the Al compound or the silicon carbide to form a stable boride during the sintering process. However, at this sintering temperature, it is unlikely that the grain growth proceeds too much.

It is preferred to pulverize the starting powder to a level of not larger than $0.8 \mu\text{m}$, so that at the time of sintering it under a pressure of not higher than 10 atm, the reactivity will be high, the liquid phase will be readily formed, and even when the grain growth proceeds, it is unlikely that coarse grains as large as more than $100 \mu\text{m}$ will form, and it is usually possible to control the grain size to a level of not larger than $30 \mu\text{m}$. It is advantageous to conduct the sintering at a pressure of not higher than 10 atm, since the densification can thereby be facilitated, and a complicated large size shaped product can be sintered in a furnace having a simple structure. It is particularly preferred to conduct the sintering under a pressure at a level of atmospheric pressure or under reduced pressure.

If the sintering temperature is lower than 1800°C , the formation of the above-mentioned liquid phase will be less, and the sintering will not proceed. The sintering temperature is preferably at least 1900°C , whereby the density of the sintered article will be high. On the other hand, if the temperature exceeds 2300°C , the reaction of silicon carbide with the liquid phase will be vigorous, and the decomposition proceeds. The sintering temperature is more preferably not higher than 2200°C .

As the non-oxidizing atmosphere, N_2 or Ar is preferred. However, it may be an atmosphere composed of or containing H_2 , CO or NH_3 .

The non-oxidizing atmosphere preferably contains a vapour of Al and/or an Al compound. Namely, it is thereby possible to prevent or control the evaporation of a part of the Al and/or the Al compound in the green body during the sintering operation.

In the process for the production of a silicon carbide sintered article according to the present invention, the sintered article thus obtained is preferably subjected further to heat treatment in a non-oxidizing atmosphere under a pressure of at least 20 atm at a temperature of from 1800 to 2300°C . By such heat treatment, for instance, a sintered product having a density of about 90% (relative to the theoretical density, the same applies hereinafter) obtained by the first stage sintering can be densified to a density of at least 95%, whereby the strength and the corrosion resistance will be improved.

The pressure of at least 20 atm is intended to facilitate the densification. However, if the pressure exceeds 3000 atm, the container is required to be scaled up to an impractical level. The pressure is more preferably from 50 to 2000 atm. The temperature of at least 1800°C , more preferably at least 1900°C , is intended to facilitate the densification by forming the liquid phase again. The upper limit of 2300°C , preferably 2200°C is meant to prevent the decomposition of the sintered material. The non-oxidizing atmosphere is preferably N_2 or Ar. However, it may be an atmosphere composed of or containing H_2 , CO or NH_3 . Further, the non-oxidizing atmosphere for such heat treatment, may contain a vapour of the Al and/or the Al compound.

The sintered article thus prepared may be employed as it is, or after machined into a predetermined shape. The sintered article of the present invention may preferably be prepared by a so-called pressureless sintering method without relying on the hot pressing method. Therefore, it is possible to obtain not only an article having a simple shape but also an article having practically any desired shape including a complicated shape. Further, also with respect to the size, there is no particular restriction on the apparatus as in the case of the hot pressing method, and therefore a large size product can readily be obtained.

The silicon carbide sintered article of the present invention is characterized in that it is obtainable by a so-called pressureless sintering method by using highly pure fine powder starting materials and by using Al and/or an Al compound as a sintering agent, and it has a specific microstructure, high strength, high fracture toughness, high thermal shock resistance and relatively superior oxidation resistance. Therefore, it can be used for various high temperature structural materials. By virtue of the excellent corrosion resistance, particularly the excellent corrosion resistance against iron, the silicon carbide sintered article of the present invention can be used as a structural material which is brought in contact with a high temperature molten metal or a high temperature iron (or steel) material. Among the silicon carbide sintered articles of the present invention, those containing a relatively large amount of Al_2O_3 or AlN , have an electric resistance at 15°C of at least $10 \Omega\text{cm}$, and the temperature coefficient of the electric resistance is negative, thus indicating characteristics of a semiconductor. Therefore, if their surface is oxidized, they can be used as good insulators. Thus, they can be used also as semiconductors or insulators useful at high temperatures.

The silicon carbide sintered articles of the present invention are useful for rollers for continuous casting, conveying rollers, skid buttons or skid rails for a heating furnace for iron or steel, skid buttons or skid rails for a heat treatment furnace for iron or steel, parts for blast furnace, converter, open-hearth furnace or electric furnace, parts for contacting molten iron or steel, protective tubes for thermocouples, stirring vanes, filters, etc.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by these specific Examples.

Examples

As starting materials, (1) light green α -SiC having a purity of at least 98% and an average particle size of $0.3\mu\text{m}$ or light brown α -SiC having a purity of at least 98% and an average particle size of $0.3\mu\text{m}$, (2) α - Al_2O_3 having a purity of at least 98% and an average particle size of $0.5\mu\text{m}$ or Al having a purity of at least 98% and an average particle size of $0.8\mu\text{m}$ and (3) TiB_2 , ZrB_2 , HfB_2 , V_3B_4 , Nb_3B_4 , TaB, CrB_2 , MoB_2 or WB_2 having a purity of at least 98% and an average particle size of $0.5\mu\text{m}$, were used. These starting materials are weighed in the weight proportions as identified in Table 1, and mixed in a wet mill. Each mixture thus obtained was molded into a green body having a size of $70 \times 40 \times 10\text{ mm}$ by isostatic press under 2000 kg/cm^2 .

In a graphite container having a volume slightly larger than the size of the green body, a powder mixture of SiC powder and Al_2O_3 powder was put, and the green body was embedded in this powder mixture and sintered under the sintering conditions as identified in Table 1. The powder mixture was prepared by mixing α -SiC having an average particle size of $1\mu\text{m}$ and α - Al_2O_3 as identified in the above (2) so that the weight ratio of the SiC and the Al component would be the same as the weight ratio in the green body. Test pieces were prepared from the sintered body thus obtained, and subjected to various tests. The test results are shown in Table 1.

Example 3 shows a sintered article which was obtained by sintering under the sintering conditions as identified in Table 1, followed by heat treatment in an argon atmosphere under 80 atm at 1950°C for 2 hours. In Examples 15 and 16, no boron compound was added. Example 17 shows a hot-pressed article having a thickness of 10 mm which was obtained by hot pressing under a pressure of 350 kg/cm^2 in an argon atmosphere under atmospheric pressure by means of a graphite die having a diameter of 60 mm.

The sintered article obtained in Example 1 had a composition comprising 53.4% of Si, 23.6% of C, 2.75% of Al, 13.5% of Ti, 5.86% of B and 0.89% of O, from which it was found that the Al content was 3.6% and the TiB_2 content was 24.7%, relative to SiC, respectively.

The sintered article obtained in Example 9 had a composition comprising 52.6% of Si, 22.6% of C, 3.07% of Al, 18.0% of Ta, 1.01% of B and 2.72% of O, from which it was found that the Al content was 4.1% and the TaB content was 24.0%, relative to SiC, respectively. Further, in each of Examples 1 and 9, the sintered article had a microstructure wherein elongated and/or plate-like grains of silicon carbide having a major axis of from 5 to $20\mu\text{m}$ and an aspect ratio of from 3 to 6 are intercrossed. The sintered articles obtained in Examples 2 to 8 and 10 to 16 had substantially the same compositions as the respective green bodies, like in Examples 1 and 9 and their microstructures were similar to the microstructure of the sintered article obtained in Examples 1 and 9. The microstructure of the sintered article obtained in Example 17 was composed of equiaxed grains having a grain size of from 1 to $5\mu\text{m}$.

In Table 1, the flexural strength was measured by a three-point flexural test with a test piece having a cross-section of $3 \times 3\text{ mm}$, a span of 20 mm and at a cross head speed of 0.5 mm/min . The value of fracture toughness (K_{IC}) was measured by a chevron notch method.

In the iron piece-contacting test, an iron piece was fit on the surface of a test piece having a size of $20 \times 20\text{ mm}$ in atmospheric air at 1200°C and left for 48 hours, whereupon the degree of erosion was measured.

As described in detail in the foregoing, the present invention provides a silicon carbide sintered article having the merits of silicon carbide such as high strength, high hardness and high heat resistance, and high corrosion resistance of a boride, wherein a sintering agent containing aluminum is effectively used to obtain high toughness, whereby problems which used to be involved at the time of the contact with high temperature iron or steel materials can be solved. Thus, the present invention provides a new material useful in a wide range of industrial fields.

Further, the sintered article of the present invention has a microstructure which is hardly obtainable by the conventional hot pressing method. It has a technical feature in that it is obtainable by a process of pressureless sintering by using fine powder starting materials and a sintering additive containing aluminum. Further, the present invention provides a technology which contributes to the development of industry, whereby a large size product or a product having a complicated shape can be produced constantly at a low cost taking the practical advantage of the pressureless sintering method.

TABLE 1

		SiC	Al or Al compound			Boron compound		Sintering conditions				
5	Example No.	Crystal form	Weight	Type	Weight as calculated as Al	Type	Weight	Atmosphere and pressure (atm)		Temp. (°C)	Time (hr)	5
10	1	β	100	Al	4	TiB ₂	25	Ar	1	2000	2	10
	2	β	100	Al ₂ O ₃	4	TiB ₂	28	Ar	1	2000	2	
	3	β	100	Al ₂ O ₃	4	TiB ₂	25	Ar	1	1950	5	
	4	β	100	Al ₂ O ₃	7.5	ZrB ₂	25	Ar	1	2000	1	
	5	α	100	Al	7.5	ZrB ₂	28	Ar	1	2000	2	
15	6	α	100	Al ₂ O ₃	10	HfB ₂	22	Ar	1	1950	10	15
	7	β	100	Al	7.5	V ₃ B ₄	12	Ar	1	2000	2	
	8	β	100	Al	10	Nb ₃ B ₄	12	Ar	1	1950	5	
	9	α	100	Al ₂ O ₃	10	TaB	25	Ar	1	2050	1	
	10	β	100	Al	7.5	CrB ₂	18	Ar	1	2000	2	
20	11	β	100	Al ₂ O ₃	7.5	CrB ₂	12	Ar	1	2000	1	20
	12	β	100	Al	4	MoB ₂	18	Ar	1	2000	2	
	13	β	100	Al ₂ O ₃	20	MoB ₂	25	N ₂	1	2050	2	
	14	α	100	Al	5	WB ₂	40	Ar	1	1950	5	
	15	β	100	Al ₂ O ₃	5	-	-	Ar	1	1950	5	
25	16	α	100	Al ₂ O ₃	4	-	-	Ar	1	1950	5	25
	17	α	100	Al ₂ O ₃	5	CrB ₂	18	Ar	350	2000	1	
Relative density (%) 15°C		Flexural strength (kg/mm ²) 15°C			K _{IC} (MN/m ^{1.5}) 1400°C		Iron piece-contacting test 15°C		Degree of erosion (mm)			
30											30	
35	95	43.7			27.8		4.1		0.02			
	91	40.5			27.1		4.2		0.07		35	
	97	48.2			29.1		4.5		0.02			
	90	50.8			31.0		4.7		0.04			
	94	45.8			32.0		3.8		0.04			
40	93	47.2			31.3		3.7		0.10			
	92	40.7			28.2		4.1		0.10		40	
	90	39.6			26.8		3.9		0.10			
	92	42.1			28.6		3.6		0.10			
	92	42.3			28.3		4.3		0.07			
45	92	48.0			30.8		3.9		0.06			
	91	45.7			25.6		4.0		0.07		45	
	88	41.0			30.7		3.9		0.10			
	92	44.9			29.4		3.6		0.11			
	94	54.8			36.5		5.3		0.17			
50	98	64.7			47.8		4.1		0.15			
	98	58.5			35.2		2.7		0.06		50	

CLAIMS

- 55 1. A silicon carbide sintered article consisting essentially of silicon carbide; from 0.5 to 35% by weight, as calculated as Al relative to the silicon carbide, of Al and/or a refractory Al compound; and from 2 to 99% by weight, relative to the silicon carbide, of at least one boride selected from borides of elements belonging to Groups 4A, 5A and 6A in the 4th, 5th and 6th periods of the periodic table, wherein at least a half amount of silicon carbide grains is constituted by elongated and/or plate-like silicon carbide grains.
- 60 2. The silicon carbide sintered article according to Claim 1, which contains from 1.0 to 25% by weight, as calculated as Al relative to the silicon carbide, of Al and/or a refractory Al compound.
3. The silicon carbide sintered article according to claim 1, which contains from 5 to 49% by weight, relative to the silicon carbide, of at least one boride selected from said borides.
4. The silicon carbide sintered article according to Claim 1, wherein the boride is a boride of a Group 4A or 6A element in the 4th, 5th or 6th period of the periodic table.

5. The silicon carbide sintered article according to Claim 4, wherein the boride is TiB_2 .
6. The silicon carbide sintered article according to Claim 4, wherein the boride is ZrB_2 .
7. The silicon carbide sintered article according to Claim 4, wherein the boride is CrB_2 .
8. The silicon carbide sintered article according to Claim 1, which is a structural material for contacting a
- 5 high temperature molten metal or a high temperature iron or steel material.
9. The silicon carbide sintered article according to Claim 1, which is a skid button or skid rail for a heating
- 5 furnace or heat treatment furnace for iron or steel.
10. A process for producing a silicon carbide sintered article which comprises sintering a green body
- comprising silicon carbide, from 0.25 to 40% by weight, as calculated as Al relative to the silicon carbide, of
- 10 Al and/or an Al compound and from 2 to 120% by weight, relative to the silicon carbide, of at least one boron
- compound selected from boron compounds of elements belonging to Groups 4A, 5A and 6A in the 4th, 5th
- and 6th periods of the periodic table, in a vacuumed atmosphere or in a non-oxidizing atmosphere under a
- pressure of not higher than 10 atm at a temperature of from 1800 to 2300°C.
11. The process according to Claim 10, wherein the green body comprises from 2.0 to 25% by weight, as
- 15 calculated as Al relative to the silicon carbide, of Al and/or an Al compound.
12. The process according to Claim 10, wherein the green body comprises from 5 to 49% by weight,
- 15 relative to the silicon carbide, of at least one boron compound selected from said boron compounds.
13. The process according to claim 12, wherein the boron compound is a boride.
14. The process according to Claim 13, wherein the boride is TiB_2 .
- 20 15. The process according to Claim 13, wherein the boride is ZrB_2 .
16. The process according to Claim 13, wherein the boride is CrB_2 .
- 20 17. The process according to Claim 10, wherein the silicon carbide has an average particle size of at most
- 0.8 μm .
18. The process according to Claim 10, wherein the Al and/or the Al compound and the boron compound
- 25 have an average particle size of at most 10 μm .
19. The process according to Claim 10, wherein the non-oxidizing atmosphere contains a vapour of the
- Al and/or the Al compound.
20. The process according to Claim 10, wherein the green body is sintered in a vacuumed condition or in
- a non-oxidizing atmosphere under a pressure of not higher than 10 atm at a temperature of from 1800 to
- 30 2300°C, and then subjected to heat treatment in a non-oxidizing atmosphere under a pressure of at least 20
- 30 atm at a temperature of from 1800 to 2300°C.
21. A silicon carbide sintered article, substantially as described.
22. A process for producing a silicon carbide sintered article, substantially as described.

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